THE APPLICATIONS OF CHEMICAL ANALYSES OF SEDIMENTS AND SOILS IN THE ASSESSMENT OF ENVIRONMENTAL QUALITY

September, 1975

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Ontario

Ministry of the Environment

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THE APPLICATIONS OF CHEMICAL ANALYSES OF SEDIMENTS AND SOILS IN THE ASSESSMENT OF ENVIRONMENTAL QUALITY

By:

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Ontario Ministry of the Environment

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ABSTRACT

The Applications of Chemical Analyses of Sediments and Soils in the Assessment of Environmental Quality

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Recent findings on the significance of various chemical and physical parameters in sediments and soils are reviewed, particularly with reference to toxic metals. The concept of natural and man-made "sinks" for toxic metals in the environment is explored. Some problem areas associated with operational and abandoned mine sites and dredging activities are discussed.

Analytical procedures used by the Ontario Ministry of the Environment, Toronto, for the analysis of metals and nutrients in sediments, soils, mine tailings, etc. are described. Various preparation procedures are used, ranging from aqua regia leach to extraction with weak acids. Analytical finishes include flame and non-flame atomic absorption spectrophotometry. Emission spectrograph procedures are currently under development.

Some of the programs with which the Laboratory is associated, such as the International Joint Commission, are discussed.

Sediments and soils play important roles in the environment as reservoirs for nutrients and toxins for animal and plants, sites for detoxifying mechanisms and, in the suspended form, provide major transportation routes. As key stages in aquatic and terrestial food chains inorganic and other toxins in sediments and soils are significant in biological concentration in each chain. eventually affecting the health of man.

Copper and zinc are the most common fresh water pollutants in Canada with mercury severe locally (Sprague 1975). The metals accumulate in aquatic organisms, especially invertebrates, with concentration factors of 1000, 40,000 and 100,000 for copper, zinc and mercury, respectively (Chapman et al, 1968). Freshwater plants also have concentration factors of 1,000 x for copper and mercury and 4,000 for zinc.

Metals can also concentrate in terrestial plants through "luxury" consumption.

Various plant species can accumulate different trace metals when in abundant supply. For example it has been found in solution culture work that turnip leaves can contain 8,000 ppm Mn, 4,000 ppm Mo, 1,500 ppm Zn and 1,000 ppm B. (Beeson and Lyon, 1948). Only iron and copper were rejected by the plant. The tomato can also take up high concentrations of metals into the leaflets. Hickory leaves can accumulate up to 5,000 ppm barium and 500 ppm lanthanum and yttrium in the leaves (Cannon, 1969). Astragalus is a concentrator of selenium (Beath et al,1934) and sweet clover of boron. The hazard exists, therefore, that the health of animals or man consuming such plants

could be affected. The known or suspected effects of anomalous concentration of trace elements in plants and animals, including humans,and their geochemical distribution has been recently reviewed (National Research Council (U.S.) 1974). Safe limits for human consumption have been defined (Health Protection Branch, 1975), subject to review.

TOXICITY

Toxicity varies with species of plant or animal, weight, age, health and other factors in the environment surrounding the individual organism.

Some metals can have toxic effects on the soil microbial populations. Silver and mercury were the most toxic of seventeen metals tested at 1 ppm as measured by carbon dioxide evolution and total numbers of bacteria, fungi and actinomycetes (Drucker et al, 1974). Dehydrogenase activity was affected by mercuric ion, depending on the clay and organic matter content (Linsay, 1975). The rate of pesticide bio-degradation was similarly affected by Hg^{2+}.

Symbiotic nitrogen fixation of nitrogen by legumes can be seriously inhibited by only 0.5 ppm mercury and 1 ppm zinc and cadmium in liquid growth media (Linsay, 1975).

Soil pH is predominant in control of metal toxicity to plants. Soil organic matter content and nutrient status, especially the availability of phosphate, are also important (Chaney, 1975). Plant rooting depth and annual vs perennial life cycles influence apparent toxicity.

An understanding of physical, chemical and biological interactions and their implications is necessary in order to use or develop the most suitable analytical method for any specific problem in environmental control.

METAL INPUT

It has become almost universally recognised that civilized man through his every day activities of living and industrial operations has had major impact on the environment. Sewage can be a source of toxic metals concentrated in sewage sludge (Swaine, 1962). Use of sewage sludge and other fertilizers, pesticides and herbicides, in addition to inputs from industry can lead to accumulation of harmful metals in human food materials (Schafer and Kick, 1970).

Construction operations, other earth moving operations (such as strip mining) and poor agricultural practices can lead to erosion of unstabilized slopes and high suspended solids in surface run-off. Buildings, roads and parking lots interfere with infiltration of rain water and also increase run-off and suspended solids content.

Input to the system also originate from emissions from municipal and industrial power and heat generating stations, building heating systems and combustion engines.

There is also input to the environment from natural sources, such as weathering processes, dissolution of mineral anomalies, volcanic action and precipitation. There is also some contribution through lightning(principally nitrates).

Wood (1974) has noted that biological methylation can occur not only with tellurium, selenium, arsenic and mercury but possibly tin, palladium, platinum, gold and thallium.

Toxicity is highly dependent on chemical form of an element. Arsenite is much more toxic than arsenate, which in turn is more toxic that organic arsenicals or metallic arsenic.

ROLE OF THE CHEMIST

The chemist can play a role in helping to determine the severity of pollutant input, potential for transport and release, and routes to detoxification.

It is becoming increasingly realized that biological activities are closely inter-related with chemical reactions. "Total" chemical composition is often less important than the fraction available or toxic to the biota.

Analysis of the sample as a whole is becoming less significant than analysis of selected size, fractions, nodules or layers in sediments and soils, parts of plants or animal organs.

The concept of available (extractable) nutrients has been widely used in terrestial plant metal uptake studies for many years and is now being increasingly applied in environmental chemistry. Analysis of "total" constituents still has some significance as an indication of potential long term contaminant and mass balance studies.

Transportation of natural and man-made potential pollutants occurs in gas, liquid and suspended particulate phases. Various mechanisms exist in nature to help prevent build-up to toxic concentration, such as by attenuation, oxidation, reduction, chelation or conversion to insoluble forms.

Chemical and biological exchange inter-relationships exist between air and water masses and terrestial and aquatic systems. Sediments,soils and large air and water masses can be regarded as sinks permitting slow release to the environment. ? they are the environment!

Natural "sinks" occur in large water masses, sediments, aquatic fiora and fauna and terrestial animals, vegetation and soil, from which there is slow release back to the environment

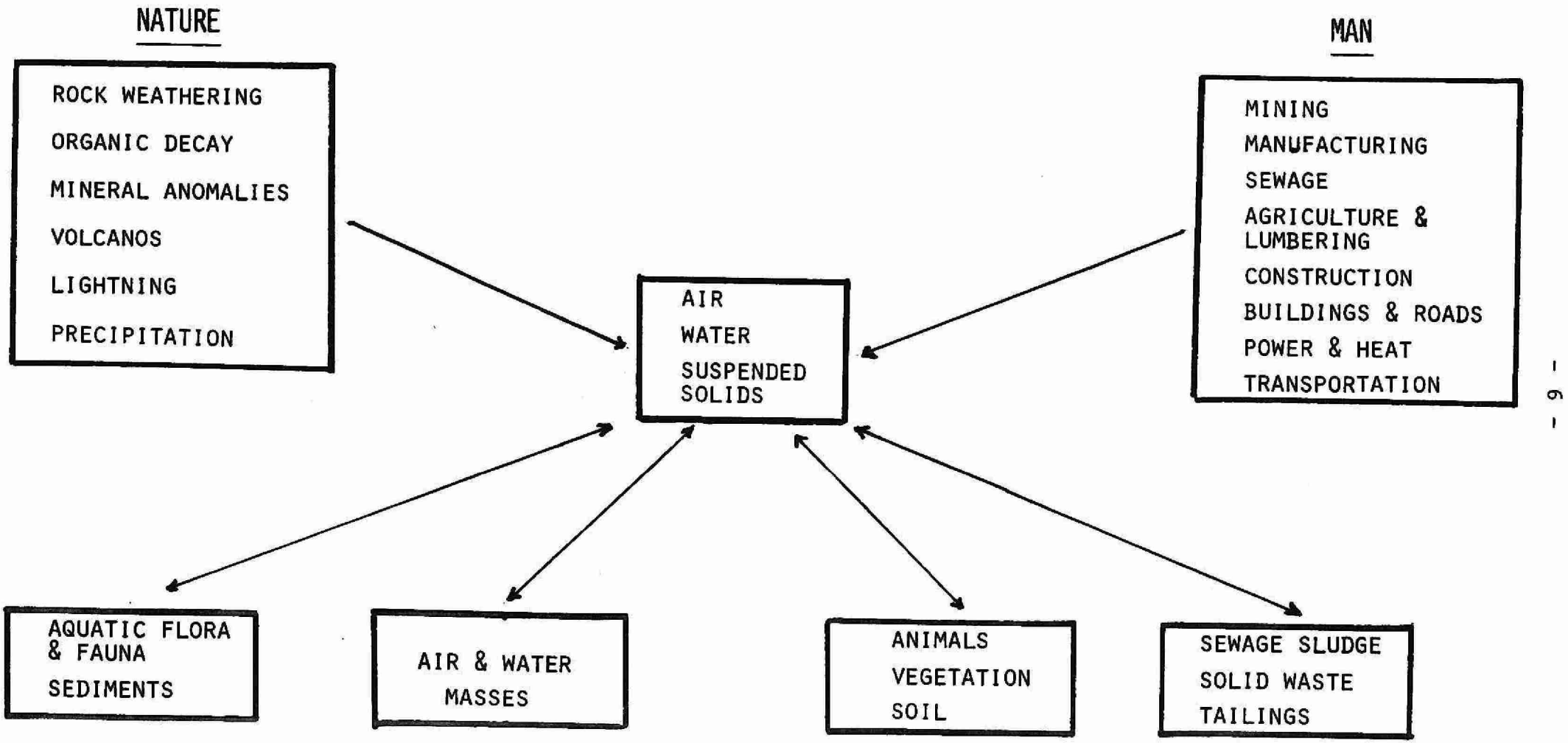
Pollutants introduced by man can also be diverted to man-made sinks, such as sewage sludge, inert solid wastes and mine tailings and industrial effluent settling ponds.

Care must be taken that materials immobilized in sediment sinks are not mobilized into water or air through disturbances such as by dredging, tailing dam rupture, blowing dust or incineration. Particulates suspended in water or air provide major transportation routes for pollutants.

WASTE WATER DETOXIFICATION

The detoxification of municipal waste water can be

POLLUTANT SINKS



cited as an example of "sink" operation. Wastewater is a major source of heavy metal contamination (Helz et at, 1975). Rapid decrease in concentration of Zn, Cu, Pb, and Cd below the outfall into Black River, Maryland was attributed to processes other than dilution, such as adsorption, precipitation, colloidal flocculation or biological uptake scavenging the metals from the water and depositing them in the sediments. Intense algae blooms were noted with day time pH often above 9.0 compared with average effluent pH of 6.9 leading to rapid deposition of trace metal hydroxides, carbonates or phosphates, and possibly increased sorption on organic and inorganic particles. Algae have also been found to concentrate heavy metals and as they die and sink carry the heavy metals into the sediments (Martin and Knauer, 1973). Cadmium appears to remobilize from the sediment possibly by cation exchange, or aging and decay of organic material, or solubilization as aqueous comlexes (Helz et al, 1975)

Acidity and colloid content,both inorganic (clays) and organic (humic material), are important factors governing metal solubility, exchange and mobility.

Total soluble metals in soil (and sediment) are made up of simple ions, hydrolysis species, complexes and chelated species (Lindsay, 1975). For metals with more than one valence state, solubility and mineral transformations are affected by redox state. Measurement of ion activities can be useful.

Initial contact of water soluble metals with soil or sediment, particularly under basic conditions, normally results in precipitation, first highly amorphous with large surface area, followed by decreased solubility as it becomes more crystalline. Surface adsorption and ion exchange reactions occur (Wentink and Etzel, 1972). Soluble or insoluble complexes can be formed with organic matter leading to either mobility or sinks, respectively. Mercury and selenium can form volatile compounds.

The importance of pH in controlling concentration of soluble species is clearly evident.

Aluminum becomes much more soluble (and toxic) at low pH. Similarly, zinc, iron and manganese becomes more available to plants under acidic conditions. On the other hand, selenium has low solubility in acid soils.

ORGANIC MATTER

The solubility of heavy metals in soils is greatly affected by natural organic chelates (Schnitzer and Khan, 1972, Langford and Gamble. 1974).

It has been found that 99 per cent of the copper in soil solution is chelated (Hodgson et al, 1965). Chelates of cobalt, manganese, zinc and iron have also been studied (O'Connor et al, 1971).

The distribution of Fe^{3+}, Zn^{2+}, Ca^{2+}, and H^{+} on EDTA (ethylene diamine tetraacetic acid) simulating natural chelates was calculated theoretically by Lindsay and Norvell, (1969) and confirmed experimentally by Lindsay (1975).

Chaney et al(1972) studied iron uptake by plants from ferric chelates and showed that there is a complexity of exchange and redox of ferric and ferrous chelates. At pH ≥6, Fe EDDHA would not release FE^{3+} rapidly enough to support plant growth. Only by reduction to ferrous EDDHA was iron rapidly exchangeable and available to plants. Bacteria are known to produce strong chelators which form slowly exchangeable iron chelates (Emery, 1974). Unstable organic matter, such as digested sewage sludge, may allow bacterial production of chelators (Chaney, 1975)

Some plant species release reducing agents, principally polyphenols, under condition of iron deficiency (Brown and Ambler, 1973).

Jackson (1975) reviewed the role of humic matter in soils and sediments in metal transport. Humic carboxyl and phenolic groups chelate a wide range of metals either releasing them as water soluble organic complexes under conditions in which they would otherwise be precipitated as sulphides, hydroxides or carbonates (Rashid and Leonard, 1973) or concentrating them in humus rich bottom sediments.

Humic complexes of iron and aluminum bind phosphate (Schnitzer, 1969). Boron, molybdenum and vanadium are also fixed by organic matter (Szalay & Szilágyi, 1967).

Humic matter also has an affinity for clay minerals, ferric oxyhydroxide and calcium carbonate as well as non-humic organic compounds. Correlations have been found between copper, zinc and nickel with organic carbon, manganese, and iron oxides and clay content (Shimp et al, 1971, Hutchinson and Fitchko, 1974).

Humic matter helps to make nutrient cations such as Fe^{3+} available to algae (Schnitzer, 1971) and assists detoxication by scavenging heavy metals and man-made organic pollutants.

If metal-humate complexes enter zones with increasing pH they start to disintegrate liberating metal ions. In anearobic sediments they will then react with H_2S to form sulphides (Pauli, 1975) often as "early diagenetic" sulphide spherules.

Organic matter extracted from soil can react with Al to form both water soluble and insoluble complexes (Schnitzer and Skinner ,1963).
Addition of organic matter such as alfalfa meal, to acid soil reduces exchangeable Al (Hoyt and Turner, 1975).

Pauli (1975) has shown that humic materials form sequestrates with metals under acid conditions. These complexes disintegrate under neutral or alkaline conditions and the liberated metals then react with sulphide.

SOME METALS OF ENVIRONMENT SIGNIFICANCE

CADMIUM

Cadmium is toxic to man and other living organisms in all its chemical forms (Copernauer et al, 1973). Zinc and cadmium are related geochemically and competitively in biological systems. The Zn/Cd ratio is important in food, ranging from 85 to 123:1 in institutional diets in the U.S. (Murthy et al, 1971)

Cadmium is normally less than 1 ppm in soils (usually up to 0.5 ppm). Chinese cabbage contained 41 ppm

near a large zinc smelter in Japan with 20-88 ppm in the soil(Kobayashi, 1972). Similar findings were made by other observers (Lagerwerff et al, 1973; Buchauer, 1973).

Near a battery plant, oat shoots contained 16-19 ppm with 46 ppm in the soil whereas the control was 0.51-0.86 ppm Cd in soil and 1.3 ppm Cd in the shoots (John et al, 1972). Cadmium concentration is often high in sewage sludge; however, conflicting results have been obtained on its uptake from plants grown on soil treated with sludge. In one test, a significant increase in Cd in soybean was obtained in soil treated with sludge containing 227 ppm (dry wt.) Cd over three years (Jelinek, 1973).

Cadmium is adsorbed on soils according to soil Langmuir adsorption isotherms (John, 1972).

ZINC

Zinc is less important toxicologically, because of the wide range between normal environmental levels and toxic levels. It is normally found in high concentration in association with lead and cadmium in soils close to smelters. "Availability"of the zinc present in the soil varies for different species of plants. Similarly, in animal nutrition "plant" zinc is less absorbable because of the formation of insoluble phytates (O'Dell and Savage, 1960) whereas soluble chelates may be formed with "animal" zinc , such as with amino acids (Evans et al, 1974).

Zinc is more available to plants under acid

soil conditions than under basic conditions as discussed earlier (Miller et al, 1964). Clay, organic matter and cation exchange capacity also influenced the adsorption of zinc (Tan et al, 1971). In calcareous soils the carbonate equivalent and organic matter content influenced the Langmuir adsorption maximum for zinc (Udo et al, 1970).

ALUMINUM

Aluminum is present in large concentrations in soils and sediments, principally in the form of relatively insoluble alumino-silicates. Under acid conditions, some of the aluminum can become soluble leading to toxic conditions, particularly in an inadequate supply of organic matter (King et al, 1974; Thomas, 1975). This aspect is discussed in more detail elsewhere in this paper.

LEAD

It has been calculated that 180,000 tons of lead-containing fuel is released into the environment each year in the U.S.constituting 98 percent of all listed lead emissions (Committee on Biologic Effects of Atmospheric Pollutants, 1972). Lead in Illinois farm soil has increased from 12 ppm to 25 ppm over the past 40 years (Snyder et al, 1971). Residential areas in larger cities have an average concentration of lead in soil of 1635 ppm with 2413 ppm in commercial areas (Committee on Biologic Effects of Atmospheric Pollutants, 1972, p.30).

Lead in soil is relatively unavailable to plants as shown by tracer studies (Committee on Biologic Effects of Atmospheric Pollutants,1972,p 30). Lead falling on plant leaves may be bound by local ligands and hence cannot be washed off (National Research Council, 1974).

Lead shot pellets have been found to cause enormous casualties among ducks by lead poisoning (IJC, 1974).

Lead molybdate($PbMoO_4$) is an important reaction product controlling the solubility of molybdenum in soil (Lindsay, 1975). MoO_4^{2-} was controlled by Pb^{2+} activity which in turn was controlled by SO_4^{2-}, PO_4^{3-} or CO_3^{2-} depending on pH.

COPPER AND MOLYBDENUM

Copper is highly toxic to algae. The addition of only 5 ug/l to Lake Ontario water depressed photosynthesis by 50 percent (Chan et al, 1970). Ligands in natural waters can mask added Cu^{2+} ions reducing their toxicity (Gächter et al, 1973).

High levels of copper and molybdenum from atmospheric fall-out causing injury to plants have been noted (Cannon and Anderson, 1971) with highest levels near smelters.

There is an interaction between copper, molybdenum and sulphate. The concentration of copper in the liver correlate with dietary intake (Underwood, 1971) and inversely by MoO_4 and SO_4.

Imbalances can result through recycling waste (animal, sewage sludge, dredging, industrial waste) because of their high trace metal contents.

CHROMIUM

Bowen (1966) reported the average concentration of chromium in U.S. soils as 100 ppm, ranging from 5-3,000 ppm with low contents in the soils of the Coastal Plain, New York and Michigan. The highest concentrations were in soils derived from basalt or serpentine such as in Maryland. In soils derived from granite and granite gneiss till the total chromium content in the A (top) horizon was 20 ppm with an acetic acid extractable content of 0.15 ppm (Swaine and Mitchell, 1960). On the other hand, although the total chromium in the A horizon of a soil derived from ultrabasic serpentine was 3500 ppm the acetic acid soluble fraction was 0.31 ppm (only 2x that from the 20 ppm total Cr soil).

Lichens have been found to accumulate up to 3,400 ppm (dry weight) Cr on soils derived from serpentine in New Zealand (Lyon et al, 1970). Allysum Markgrafi contained 10 ppm in background areas compared with 3,000 ppm above a deposit in Yugoslavia (Karamata, 1967).

Industrial pollution is probably increasing the content of chromium in water, air, soil and plants as indicated from the geographical distribution of chromium in municipal water supplies (Lieber and Welsch, ,1954). Addition of chromium to areas of low chromium may be beneficial.

Of interest is the form of chromium in its effect on man. It is an essential element and the optimal form is a yet unidentified water soluble, low molecular weight complex (Mertz and Roginski, 1971). In animals, the rate of synthesis of this compound in the intestinal flora is probably the most important factor. Determination of total chromium gives little information about its biological value (National Research Council,1974).

ARSENIC

Arsenic is commonly associated with sulphidic ores of copper and gold and becomes airborne as the oxide during the roasting process. Some soils, such as in New Zealand, are naturally high in arsenic (up to 1 per cent). It was previously used extensively in agriculture. Orchard soils in South-Western Ontario have been found to contain as much as 121 ppm (Miles, 1968). Inorganic arsenic is rapidly deactivated in soil through the formation of insoluble iron and aluminum salts.

Organic arsenicals of low toxicity such as mono- and di- sodium methane arsonate (MSMA and DSMA, respectively), cacodylic acid and arsanilic acid are also used in animal food supplements. Arsanilic acid entering soil from manure is immobilized by iron, aluminum and calcium in the same manner as arsenate and phosphate (Woolson, 1975).

Biological concentration occurs up the food chain with up to 700x in fish. Submerged aquatic plants such as

Ceratophyllum in New Zealand can concentrate 20,000x to 971 ppm (Reay, 1972).

Methylation is a significant means of transport and detoxification. It occurs extensively in the rumen of cattle and methylated forms can be found in the urine (Lakso and Peoples, 1975). Methylation in anaerobic sediments can lead to the formation of highly poisonous dimethyl arsine (Lii et al, 1973).

Fatalities have been documented for persons drinking well water containing 10ppm As as arseno-pyrites in suspension in Madoc, Ontario in 1935 (CRC Press, 1974). A correlation was obtained between the concentration of arsenic in well-drinking water up to 1.4 ppm with concentration in human hair (Goldsmith et al, 1972). There was no evidence of any specific illness.

SELENIUM

Selenium occurs principally in volcanic emanations and metallic sulphides associated with igneous activity and in biological materials such as black shales and coal. Approximately 6 times as much selenium is entering the atmosphere from the burning of fossil fuels than from mined ores (National Research Council, 1974). Selenium deficiencies in livestock are prevalent in the north-eastern U.S. with 80 per cent of all forage and grain containing <.05 ppm Se (Kubota and Allaway, 1972).

Availability to land plants depends on the chemical form of selenium which in turn is governed by pH and Eh. Elemental selenium is moderately stable and

not appreciably available. In acid soils (pH 4.5 - 6.5) selenium usually occurs as the basic ferric selenite which has very low solubility and is almost completely unavailable. In alkaline soils selenium can be oxidized to the selenate and become water soluble and available (National Research Council, 1971). Where alkaline soils are formed from parent rock containing selenium the plants may contain 0.1 to 10 ppm dry weight. If acid soils are formed plants can contain 0.02 to 0.2 ppm. Selenium accumulator plants such as Astragalus can contain from 50 to 1,000 ppm compared with 1 to 5 ppm in nearby non-accumulators.

IRON AND MANGANESE

Iron and to a lesser extent manganese are normally present in sediments and soils in major amounts and play important roles with respect to other metals.

The activity of Fe^{3+} in equilibrium with ferric hydroxide decreases 1,000x for each unit increase in pH. Hydrolysis products combine to form polymeric complexes such as $Fe_2(OH)_2^{4+}$.

It has been shown by X-ray diffraction and Mössbauer spectroscopy that the majority of iron in dried surface sediments of a wide range of Canadian Lakes consists of crypto-crystalline ferric hydroxide (Coey et al, 1974). Iron is also often present as chlorite with illite, and possibly pyrite and ferrous phosphate.

Very rapid absorption of heavy metals in sediments can occur on hydrated ferric and manganese oxides (Chen, 1972). The absorptive capacity is greater on

freshly precipitated material (Lee, 1973).

It has been shown that microcystalline hydrated iron oxides can absorb 90 to 95 per cent of mercury from a 200 ppb solution in a few days (Krauskopf, 1956).

The sorption efficiency of clays for heavy metals is probably due to iron oxide or to a lesser extent manganese oxide coating on the clay particles (Jenne, 1968).

Of interest are iron- manganese oxidate crusts at the surface of sediments, such as in Oneida Lake, New York (Dean, 1970) and several Canadian Lakes (Harris and Troup, 1969). Their formation is believed to be the result of precipitation of iron and manganese when reduced sediment interstitial (pore) water comes in contact with well oxygenated bottom waters. They are usually formed on rock cores, often in shoal areas with a slow rate of sedimentation and turbulent mixing.

Concretions in Canadian lakes have been found to consist of 15.7-35.9 per cent manganese and 11.7-40.2 per cent Fe with up to 230 ppm Co, 373 ppm Ni and 1940 Zn (Harriss and Troup, 1969). An extensive area of exploitable small ferro - manganese nodules has been discovered in the Green Bay area of the Great Lakes (Moore, 1970).

A strong correlation was obtained between iron concentration and mean grain size for Ottawa River sediments and between iron and mercury and iron and manganese (Rust and Waslenchuk, 1974). The concentration of ferrous iron and its hydrolysis products increases as the partial pressure of oxygen decreases from 1 to 10^{-40} atmospheres. Iron also forms complexes with ions such as chloride, sulphate and phosphate and organic chelates.

A correlation was found between total Fe, Mn and P in Lake Muscoka sediments, Ontario (Brydges, 1970). Similarly changes in pH and redox conditions have major effects on the solubility of manganese.

SULPHIDE

Precipitation of some heavy metal sulphides in flooded soils and sediments is an important mechanism regulating the solution concentration of S^{2-} and the metal ions Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} and Hg^{2+}. Under anearobic conditions these sulphides were found to be very stable (Engler and Patrick, 1975).

Sulphide reducing and methane producing bacteria in the bottom deposits of fresh water lakes appear to play an important role (Cappenberg, 1974). The sulphate reducers were most abundant at the 0-2 cm depth, producing H_2S, with methane producers at 3 to 6 cm depth. The sediment in the deepest part of the lake were black in colour due to precipitated iron sulphide.

PHOSPHATE

The phosphate mineral apatite ($Ca_5(PO_4)_3F(Cl,OH)$) occurs in Great Lakes post-glacial sediments. Vivianite ($Fe(PO_4)_2 8H_2O$) is important in controlling aqueous phosphate concentration and often occurs in sand size nodules (Dell, 1973). Brydges (1970) suggested iron was the most important release factor for Lake Muscoka (Ont.) sediments under anaerobic conditions. Lead phosphates are present in soils of intermediate pH, lead sulphate in very acid soils. and lead carbonate above pH 7 (Lindsay, 1973).

The presence of lead phosphate crystals in corn leaves heavily contaminated with lead was established by scanning electron microscopy with nondispersive X-ray emission (National Research Council, 1974)

DISTRIBUTION OF METALS

A. WITH PARTICLE SIZE:

Heavy metals are often associated with finer sediment grain size(Thomas, 1972; Oliver & Agemian, 1974)). In the Great Lakes, concentration and distribution of sediment bound mercury is intimately associated with sediment type (Thomas, et al, 1973; Thomas, 1974; Hartung, 1974). When corrected for the quartz content of the sediment, a realistic assessment of mercury concentration in the fine particulates was obtained (Thomas et al, 1973; Thomas, 1974). In a study of Ottawa River sediments, the sorption capacity for mercury was 99x for the 0.45 to 38 μ fraction than for sand ranging from 100 to 150 μ (Townsend et al, 1974). Wood fibres had a greater capacity for mercury than the sand fraction. Similarly, hydrochloric acid extractable cadmium and chromium were higher in the fine grained sediments of the Lower Mississippi (Hartung, 1974).

The correlation between iron concentration and grain size for Ottawa River sediment was noted earlier (Rustand Waslenchuk, 1974)

The greatest contrast between anomalously high and background levels for heavy metals was found by analyzing the -80 mesh fraction (Hawkes and Webb,

10-20 cm of lake sediment and suggested that bacteria generated gas bubbles forming extremely reactive surfaces could cause uni-directional migration of heavy metals, phosphates and nitrates.

C. SEDIMENT - WATER INTERFACE

Exchanges across the sediment-water interface are of great significance. Fresh organic matter is continually added to the sediment surface and is decomposed leaving resistant humic residues. Oxygen is required for this decomposition at a rate dependent on biological (respiration and metabolism) and chemical reactions (oxidation of ferrous iron, etc.) and diffusion, molecular within the sediment but much more rapid due to turbulence at the surface (Mortimer, 1971). The depth of the zero oxygen level (between the oxidized surficial layer and reduced sediment) a few millimetres below the surface of the sediment is critical in regulating chemical exchange. The depth of the zero oxygen level will change according to the supply of oxygen, such as during the annual overturn of a lake or stratification. The oxidized upper layer (microzone) forms an efficient trap for manganese, iron and phosphate both moving up through the sediment and scavenging metals from the overlying water (Gorham, 1958)

Iron and manganese concentration in this layer are often an order of magnitude higher than in the reduced sediments below and are often orange due to

1972; Wolfe, 1974).

Good correlations were obtained between loss on ignition (organic matter content) and per cent clay with zinc and manganese in river mouth sediments in the Great Lakes area with weaker correlations for lead, copper, nickel and mercury (Hutchinson and Fitchko, 1974).

B. VERTICAL DISTRIBUTION:

Vertical concentration for heavy metals in sediments have been noted by several observers (Shimp et al, 1971 ; Thomas, 1972; Iskandor and Keeney 1974) and were attributed to man's urban and industrial activities. However, such concentration profiles were not found in some Great lakes river mouth sediments probably because of mixing by dredging, shipping action and current action (Kovacik and Walters, 1973; Hutchinson and Fitchko, 1974).

A vertical distribution in concentration in sediment has also been noted for mercury. Over 97 per cent of the mercury present in sediments of the Ottawa River was located in the top 4 cm (Hart, 1972).

Copper and nickel concentrations were several times higher in the top of each core than in the bottom for lakes sampled in the Sudbury area in connection with a lake reclamation program (Michalski and Adamski, 1974; Scheider et al., 1975; Sadana, 1974).

Cline and Upchurch (1973) noted high concentrations of copper, mercury and zinc in the upper

ferric hydroxide (Gorham and Swaine, 1965). Metals can become mobile through chelation with humic materials (Pauli, 1975).

The presence of sulphate reducing bacteria at and just below the interface, leading to the precipitation of sulphide, was noted earlier (Cappenberg, 1974).

SOME PROBLEM AREAS I-MINING

MINING AND THE ENVIRONMENT

It has been estimated that in Ontario, 80 million short tons of waste mill tailings must be disposed of annually, preferably in engineered impoundment basins (Caplice and Shikaze, 1970). Tailings banks have to be stabilized, preferably by a self-sustaining vegetated cover, such as at INCO in Sudbury (Peters, 1968) and at the Hollinger gold mine in Timmins (Gordon, 1969).

Mine water and tailings overflows can also cause problems. Much of it can be recycled as at INCO, Sudbury. Cyanide from gold mining can be oxidized and arsenic, associated with silver ores, precipitated by liming. In uranium mining radium removal can be effected by co-precipitation with sulphate by addition of barium chloride, as at Dennison and Rio Algom Mines.

Serious problems can arise following abandonment of a mining operation.

The Ontario Ministry of Environment is monitoring arsenic leaching into the Moira River through the ground water from calcium arsenite settling ponds at the Deloro Mine abandoned in 1963 (Ministry of Environment, 1973).

Continued control was found necessary by installing lime addition facilities in addition to the existing ferrous sulphate system.

Mercury was once used in early mining processes in the recovery of silver and is causing concern today in the Lake Timiskaming area near Cobalt, Ontario.

ASSESSMENT OF MINING CONTRIBUTION

A major challenge in environmental chemistry is to determine the contribution of mining operations to pollution. Ideally pre-mining background studies should be conducted to establish base levels, often entailing analysis at trace levels. In established mining areas other methods are needed.

In the Canadian Shield area, analysis of glacial deposits, soils, sediments and water, vegetation and fish can be used. Lake sediment cores have been proposed as the ideal media for environmetal geochemistry studies (Allan, 1974). Most lakes in the Shield area studied have accumulated less than 10 cm of sediment in the past 100 years. The oldest mines in the Sudbury area have only been in operation for about 80 years, hence core samples below 10 cm reflect natural levels prior to mining in this area, allowing for diagenesis of the sediments and biological effects on mobilization and redistribution. The nickel concentration was much higher at the surface of the cores. Concentrations from deeper in the cores were often less than those for similar geologic material in uninhabited areas of Northern Canada.

The surface 5 cm of sediment from MacFarlane and Raft Lakes, 5.5 miles from Coppercliff contained 871 and 625 ppm nickel respectively. The surface 5 cm from Whitefish Lake, 8.5 miles from Coppercliff contained 348 ppm Ni. The concentration of nickel at 10-15 cm ranged from 10-40 ppm. Similar observations were made by other workers in the same area as discussed earlier (Michalski and Adamski, 1974).

Decreasing nickel concentration with depth was also found in soils contaminated by airborne pollution from the Coniston smelters (Contescu and Hutchinson, 1972); Hutchinson and Whitby, 1974, Whitby, 1974).

Copper has only been mined in the Lac Dore area of Chibougaman for the past 20 years. Unlike Sudbury sediments, no trend was observed in copper distribution down the lake sediment core possible because of the shorter time period (Allan, 1974).

Contaminated lake sediments were found downstream of base metal mining camps near Manitouwadge, Ontario, in operation only since 1957. Maximum concentrations in Manitouwadge and Mose Lake muds were, respectively, 8860 and 7120 ppm Zn, 1234 and 3480 ppm Cu and 662 and 476 ppm Pb, compared with uncontaminated sediment levels of about 150 ppm. Lakes downstream of Manitouwadge and Mose Lakes had only slightly elevated levels of copper and lead, whereas high zinc levels were found in more remote lakes (German, 1974).

ACID GENERATION IN MINING

Deterioration of aquatic ecosystems often results

from run-off of acidic water from mining operations. Oxidation of sulphide minerals generates sulphuric acid. Each molecule of iron pyrite (FeS_2) releases ferrous ion, which in turn is oxidized to ferric iron, which is hydrolyzed to ferric hydroxide,two moles of sulphate and four hydrogen ions (Stumm and Morgan, 1970). Bacterial activity accelerates acid formation (Temple and Delcamps, 1952) but also acid reduction through sulphate reducing bacteria under anaerobic conditions in the presence of organic matter (Campbell and Lind, 1969; Tuttle, 1969; King et al, 1974).

Acid mine drainage is a serious problem in Ontario, principally from untreated seepage from active tailing areas and uncontrolled seepage from abandoned sites (Hawley and Shikaze, 1971). Seepage from an abandoned tailings area in the Elliott Lake District had a pH of 2, 7440 ppm SO_4, 1450 ppm Fe^{3+} and 1750 ppm Fe^{2+} and 588 ppm Al^{3+}.

Clay minerals and alkali metal compounds such as calcium, and magnesium and manganese carbonates also help to reduce acidity (King et al, 1974). Sorption of H ion occurs on clay mineral surfaces and there is some dissolution of clay mineral such as kaolinite yielding soluble aluminum and silicic acid which contribute buffering capacity. The aluminum, in turn, will slowly precipitate as gibbsite or bayerite (Hem and Robertson, 1967). The concentration of soluble aluminum and iron is highly pH dependent, as shown from Missouri strip mine lakes with reduction in soluble Al from concentrations up to 200 mg/l at pH 3 to very low levels above pH 4(King et al, 1974). Aluminum is approximately 4 orders

of magnitude more soluble than iron over the pH range of 2 to 4, hence it has a greater potential for buffering capacity as the pH rises through sequential hydrolysis and precipitation.

Organic matter content of soils has a marked effect on exchangeable aluminum extracted by 1N KCl in acid soil helping to prevent toxicity (Thomas, 1975).

Solution of carbonates results in increased pH, decreased acidity and high concentrations of soluble Ca, Mg and Mn often noted in strip mine lakes (Campbell and Lind, 1969).

Microbial sulphate reduction is favoured by increasing the depth of organic matter to promote depletion of dissolved oxygen and accumulation of reduced products. Reduction of iron is accompanied by increased content in micro-organisms,increased sulphide concentration, formation of elemental sulphur and precipitation of iron sulphide. Sulphate reduction accelerates above a pH of 4.5 with bicarbonate formation and release of H_2S to the atmosphere. It has been suggested that controlled slow release of H_2S by adding piles of organic matter periodically to a strip mine lake is a practical route to reducing sulphate (King et al, 1974).

SOIL ANALYSIS IN RELATION TO FERTILITY OF MINE TAILINGS

An important area of concern is the establishment of vegetation on mine tailings and overburden from strip mining not only for aesthetic reasons but to reduce wind blowing. Measurement of fertility becomes very important

in terms of physical and chemical suitability of the rooting medium. Physical measurements include soil texture (mechanical analysis), structure and depth and the dependent parameters of permeability and moisture holding capacity. Chemical measurements include analysis of acidity and available macro and micro nutrients, and non-essential and possibly toxic metals.

Acidity is the main concern in Carbolithic mine soils of coal overburden of West Virginia (Smith et al, 1974). The pH at 10 inch depth was proposed as a satisfactory criterium for pH status:

Extremely acid	pH 4.0
Acid	pH 4.0 - 5.5
Neutral	pH 5.5 - 8.0

pH measurements should be made on a thin paste. A 1:1 soil/water ratio is used by the West Virginia Soil Testing Laboratory, agitating during measurement for coarse textured material (Smith et al, 1974). Soluble salts can affect pH and can be eliminated by leaching with distilled water or adding salt solutions such as 0.1N KCl and 0.01 M $CaCl_2$. Acidity is primarily due to mineral acids below pH 3.7 whereas exchangeable Al dominates acidity in the range of pH 4.0 - 5.5. Exchange acidity is that which can be replaced by a neutral unbuffered salt such as KCl with pH values approximately 0.5 units lower for acidic West Virginia mine soils (Smith et al, 1974). Titrable acidity can also be measured by titration to pH 8.2 by the $BaCl_2$-T.E.A. method which measures other components contributing to acidity (Smith et al, 1974).

Pyritic sulphur content, measured after leaching out sulphate and carbonates is most important in the consideration of toxicity or potential toxicity from acidity.

Acid Potential of soils has been determined by hydrogen peroxide oxidation (Brinkman and Pons, 1972). If the sample is pretreated to remove carbonate and sulphate, a strong correlation ($r^2 = 0.970$) was found between acidity and per cent sulphur (Smith et al, 1974).

The Acid Potential of powdered coal, and probably other materials, can be measured under carefully controlled laboratory conditions in the absence of micro-organisms using distilled water in a heated Soxhlet extractor and a peristaltic pump (Smith et al, 1974).

Determination of Neutralization Potential is important in the evaluation of mine soils and can best be measured by acid titration using a modification of Jackson's method (Jackson, 1958; Smith et al, 1974)

The Woodruff buffer method (Woodruff, 1948) has been found satisfactory in determining the immediate lime requirement of acid mine spoils in West Virginia (West Virginia University, 1971). However, if there is appreciable sulphide, such as pyrites, and there are insufficient bases present as shown by the Neutralization Potential, the lime requirement can be estimated from per cent sulphur (Smith et al, 1974). Stoichometrically, for 0.1 per cent sulphur as FeS_2, 6250 lb. calcium carbonate are required to neutralize 1000 tons material.

The Term Net Potential Deficiency (Smith et al, 1974) has been used, expressed as calcium carbonate equivalent per 1000 tons, which can be calculated by sub-

tracting the carbonate present found by titration from the maximum required (from % S). Toxic or potentially toxic material was defined as that with a pH $<$ 4.0 and a Net Potential Deficiency of 5 tons or more of calcium carbonate per 1000 tons, i.e. one acre plot layer (Smith et al, 1974).

The effect of chemical weathering on mine spoil on titratable acidity and alkalinity, sulphate and pH can be simulated in the laboratory (Smith et al, 1974). In pot tests, mixing acid sandstone mine soil with different rates of limestone, a correlation was found between sulphate S and pH, possibly because of reduced Thiobacillus activity at higher pH (Zuberer, 1972).

The physical weathering potential of rocks is important in assessing their suitability as a soil. Intact rock fragments can be shaken with 5% Calgon in distilled water for 16 hours and the resultant particles analyzed for size distribution by the hydrometer method (Smith et al, 1974).

Cation exchange capacity (CEC) can be measured by several methods such as ammonium (Jackson, 1958) or calcium (Rich, 1961) saturation or by summing exchange acidity with calcium acetate at pH 7 (Nelson et al, 1953), $BaCl_2$-TEA, pH-8.2 or N KCl (Jackson,1958) and extractable bases with acid (Nelson et al, 1953) or 1N ammonium acetate, pH 7 (Jackson, 1958). Big differences in C.E.C. on acid mine soils were obtained using the different methods (Smith et al, 1974). The latter two methods were most reliable with the difference in CEC being due to exchangeable hydrogen.

Organic carbon can be measured by converting carbon to carbon dioxide in a furnace and collecting and measuring the CO_2. The Walkley and Black chromic acid wet oxidation method (Jackson, 1958) can be used to determine readily oxidizable organic matter even in the presence of up to 50% $CaCO_3$. Recoveries of 60-86 per cent of the organic carbon are obtained. Other oxidizable material and higher oxides of manganese and reduced iron interfere. Low temperature ignition at 350 - 400 ^{o}C for 7 - 8 hours can be used. Using some West Virginia mine soils there was a high correlation (r = 0.977) between low temperature ignition and the Walkley - Black method although the results were almost twice as high (Smith et al, 1974):

Y(Walkley-Black) = 0.3079 + 0.4122 x Ignition

Loss on ignition is routinely analyzed at the Ministry of the Environment as the weight loss at 600^{o}C.

Analysis of major nutrients is also important in relation to establishing vegetation on mine soils.

Available phosphorus can be measured after acid or alkaline extraction. Acid extraction has been found to give unreliable results on alkaline soils due to solution of carbonate weakening the strength of the acid, or solution of non available apatite. On acid soils solution of iron can give erratic results (Smith et al, 1974). Sodium bicarbonate extraction has been found to relate to plant response (Olsen et al, 194; Olsen and Dean, 1965) and a satisfactory correlation (R = 0.86) with acid ammonium fluoride extractable P for acid minesoils (Smith et al, 1974).

II-DREDGING OPERATIONS

In the process of dredging large quantities of sediments can be suspended with mobilization and transport of pollutants. The EPA has defined "polluted" in terms of mercury, lead, zinc, oil and grease, total kjeldahl N (TKN) COD, and volatile solids. The MOE has defined similar parameters, more stringent for mercury and TKN (.3 ppm & 0.1%, respectively),as limits for open water disposal.

A standard Elutriate test has been developed by the U.S. Army Corps of Engineers (Keeley and Engler, 1974). The test consists of shaking the dredged material in 1:4 ratio with disposal site water for 30 minutes. Filtered receiving water (X_i) and the elutriate (X) are analyzed for the specified parameters. If $X \geq 1.5X_i$ the constituent exceeds the pollution criteria.

Most of the U.S. harbours along the Great Lakes are polluted by the EPA standard (IJC, 1974). High zinc and lead have been found in Toronto Harbour (Wilkins, 1974).

It has been found that dredging can lead to phosphorus release to the waterway, principally because of the higher phosphorus content of the interstitial water (Posner et al, 1975).

On the U.S. side of the Great Lakes, approximately 11 million cubic yards of dredged spoil must be moved each year (Hansen, 1971). All dredged material was previously disposed of in open water; in the mid 1960's, however, the U.S. Corps of Engineers and the Department of the Interior initiated an investigation into the ecological implications of open water disposal. Mercury,

specifically because of the possibility of mobility through methylation, was considered to be a serious threat.

Diking was believed to be the most practical alternative to open water disposal, although other problems can be raised such as danger to wildlife. Costs of alternative disposal can be several times that of the open water method.

M.O.E. ANALYTICAL METHODS

Sampling requirements for sediments, soils, and aqueous samples and outlines of analytical methods have been described (Ministry of the Environment, 1975).

The importance of sampling and which fraction is to be analyzed is evident for the discussion of metal distribution with particle size and depth. In a study of Lake Muscoka sediments only the top 1 cm was sampled (Brydges, 1970). Because of the well recognized wide variability in the horizontal direction (Wolfe, 1974), composite samples are often taken. Core samples of sediments are frequently collected, such as in a recent study of Hamilton Harbour, and maintained frozen until analyzed, sampling various depths down the core. Most samples are maintained at 4°C until ready to analyze.

Instrumentation available at the Central Laboratory for the analysis of industrial effluents (and sediments and soils) is discussed by Bishop and Diosady (1975).

The laboratory functioned until very recently

as a routine testing facility analyzing only the convential parameters of Loss on Ingition (LOI), total heavy metals and total nutrients (N and P). The inadequacies of these tests is now realized with the understanding that extractable or "available" metals and fertility parameters such as pH, carbonate content, organic matter, and texture have more significance environmentally. There is also an increasing demand for a wider range of metals, particularly in background surveys. There has been a large increase in the number of tests and tests per sample during the past two years dictating a need for simultaneous analysis of many elements, such as by spectrography, preferably with minimal sample preparation.

Sediment and soil samples are normally dried at 105°C, pulverized and sieved through a 1.4 mm nylon sieve. Some work has been done with freeze drying, principally to minimize the time for hand pulverizing.

METAL ANALYSIS

The dried samples are digested with 10/5 HCl/HNO_3 using two sample weights (0.50 and 1.00 gm) to help check for interferences and to improve confidence by replication. Sulphuric acid/nitric acid (5:2) is used for silver and arsenic. Present practice is to use overnight digestion at low heat in 125 ml Phillips' beakers.

Five mls of HCl are added following the digestion. Blanks and two internal reference samples are included in each run for quality control. Problems occurred due to contamination and high blanks which have been largely

corrected by protecting samples in the fumehood from contamination by a baffle and overnight soaking of glassware in 50% nitric acid.* Millipore filters were previously used by these have been replaced by filtering through paper in long stemmed glass funnels, both quicker and less subject to contamination. The volume is then made up to 50 mls and the mouths of the tubes covered with Parawax.

Previous practice was to ash all samples at 600°C prior to digestion. However, it was realized that there could be serious losses of volatile metals such as lead and cadmium. Low temperature ashing (LTA) was evaluated as a means of removing organic matter, obtaining an ash which could be readily extracted with cold nitric acid with minimum loss of volatile metals. The method worked very satisfactorily for biomaterials such as fish but was unsuccessful for sediment, principally because of incomplete ashing, small sample size (0.1 gm) and the long time required. It was planned to obtain an LTA with a vibrator system.**

It is recognized that these extractions are not complete (van Loon and Lichwa, 1973) as metals bound in minerals are not measured (Anderson, 1974). Lithium tetraborate fusion was previously practiced in this laboratory but has the disadvantage of small sample size and hence low sensitivity, high reagent blank contribution and high salt content interferences in AAS.

Pressure digestion in a Teflon lined bomb with HF using the method described by Davison et al (1974) was found very satisfactory for fly ash and is being

* Recently found unnecessary following adoption of washing in a Mielé washer

** Obtained since meeting and currently being evaluated.

evaluated for sediments. Heavy metal concentrations approximately 2 times those for aqua regia digestion were found for fly ash using the HF bomb method compared with aqua regia digestion, indicating the high proportion of metals locked into silicate minerals in this type of material.

Most analyses are conducted by atomic absorption spectrophotometry using either a Varian AA-5 or M1250, Perkin-Elmer 503, or IL 251. The need for background correction is becoming increasingly evident (currently used for Pb, Cd, Ni, Mo*, Sn and Co).

Iron is measured at the less sensitive wavelength of 386 nm using nitrous oxide-acetylene, which gives a linear response up to 1000 ppm.**

Arsenic is normally analyzed after sulphuric-nitric digestion by the automated boro-hydride non-flame (quartz tube) AAS method developed by Vijan and Wood (1974). If aqua-regia digestion is used, sulphuric acid is added prior to hydride generation.

Sulphide is analyzed by a distillation-molybdenum blue procedure, modified by this laboratory (Darcel and S. Ali, 1974). A promising wet method for total sulphur was investigated based on HNO_3($HClO_4$/ $MgNO_3$ oxidation followed by Hl reduction to H_2S (Norwitz, 1971) but was subject to high blanks.

Extractable metals have been analyzed by shaking the sample with N ammonium acetate, adjusted to pH 4.8 with acetic acid, in 1:5 ratio for 30 minutes on a wrist action shaker. The extraction is followed by filtration or centrifugation and aqua regia digestion of the filtrate

* Currently being investigated.
**More recent practice is to use 248 nm and high dilution using an auto-analyzer system.

prior to metal analysis.

Study is in progress on a satisfactory method for selenium. The hydride-non flame AAS method developed by Vijan and Wood (unpublished) has shown considerable promise for water samples and will be evaluated shortly for sediments. The standard addition technique would have to be used for sediment samples to allow for interferences such as copper. Most important appears to be a boil-up step with HCl following ~~and~~ acid digestion.

A gas chromatograph method has been found to give good agreement for selenium in NBS fly ash and hence is expected to satisfactory for sediments, although more time consuming that the hydride method.

At present, the Jarrell Ash emission spectrograph has not demonstrated satisfactory agreement with AAS analysis for sediment and soil samples.*

Semi-quantitative scan by plate read-out for metals using pulverized sample blended with graphite and lithium carbonate can be conducted followed by ~~AAS~~ ES analysis. Unfortunately, this method is time consuming and work is proceeding on trying to improve agreement between AAS and Emission Spectrograph with direct read-out on digested samples by using larger sample size and concentration to permit analysis in the linear range of the instrument. It is planned to instal an inductively coupled plasma torch system (as currently used by the U.S. Environmental Protection Agency) in early 1976 to increase sensitivity.

It is hoped that the spectrograph will be able to take the place of AA5 for most analyses because of its potential capability of simultaneous analyses of many

* More recently encouraging correlations have been found for some elements.

elements by direct reader (currently 32 channels).

Present practice is only to analyze those parameters requested by the sender; however, with the spectrograph it will be possible to analyze other environmentally important metals at no additional expense and alert the sender to pollutants other than those suspected.

MAJOR NUTRIENTS ANALYSIS

Analytical procedures for total N and P, and Loss on Ignition (LOI) at 600°C are described by Brydges (1970). Iron and manganese were previously analyzed colorimetrically but more recently by flame AAS.

Ignition loss at 350-400°C has been found to give a good indication of organic matter content analyzed by the Walkley-Black method (Smith et al 1974) as discussed earlier. Brydges (1970) found correlations between LOI at 600°C and total Kjeldahl N and dry weight of sediment per unit volume in some northern Ontario lakes. It is planned to evaluate LOI at 600°C vs 350°C to determine the contribution of carbonate.

Chemical Oxygen Demand (COD) tests are also conducted on sediments using a modified Walkley-Black chromic acid procedure.

There has been little success to date with evaluation of Total Organic Carbon (TOC) at MOE by high temperature combustion, such as the Carbo-Erba method used at the Canadian Centre for Inland Waters.

Measurements are made of other solubles as required for the disposal of dredge spoil.

Little progress has been made with the characterization of organic matter and organo-metallic complexes. A Organo-Metallics laboratory is currently being equipped at the MOE Central Laboratory to investigate the role of these compounds in sediments and soils.

There have been few requests for Acid Potential and Carbonate analyses although the importance of these tests in northern Ontario mining areas is recognized.

Carbonate can be analyzed by the Chittig method. More rapid methods are being investigated.

Extractable phosphorus is normally analyzed by shaking with 0.5 N sulphuric acid in 1:5 ratio for 30 minutes.

The "Triple-A" test (Aerobic-Anaerobic) was developed for wet sediment measuring phosphorus extracted after 7 days with distilled water, using sodium sulphite to remove oxygen for the "anaerobic" test (Bennett and Brydges, 1969). This test was used in a Muscoka Lake study in 1970 but has not been used more recently.

PHYSICAL ANALYSES

Mechanical analyses of soils in sediments are currently performed by a combination of dry sieving and sedimentation using the Bouyoucous hydrometer method. Measurements are also made of the Atterburg plasticity limits and permeability.

SOME ACTIVITIES OF THE SEDIMENT & SOILS LABORATORY

Samples are received from all over Ontario,

many of them in connection with major projects such as the International Joint Commission, establishment of pre-mining background levels and industrial waste monitoring. Some recent programs are discussed below.

INCO MINE TAILINGS VEGETATION STUDY

An experiment is in progress on the effect of the addition of sewage sludge from secondary treatment on the stabilization of tailings by vegetation at the International Nickel Co., Sudbury. Field work was undertaken by the Biology Department of Laurentian University from 1973 on with some back-up heavy metal analyses by the Ministry of the Environment and nutrient analyses at the University of Guelph. pH values at the surface usually ranged from 5 to 6 and pH 4 lower in the soil profile. (G.M. Courtin, Unpublished data).

In analyses by MOE (Unpublished) wide variations were found in concentrations of copper, nickel and aluminum in 1:5 ammonium acetate pH 4.8 extracts.

Titanium was below the detection limit (0.3 ppm) and zinc in low concentrations (usually below 1 ppm). Further work is required to determine if the concentrations of heavy metals noted above are toxic and if there is uptake into the plants.

Measurements would also probably be worthwhile of parameters such as Acid Potential and calcium carbonate requirements. Permeability was reduced during the test period but could be restored by cultivation. Mechanical analyses, measurement of total organic matter content and

and characterization of the humic material would be of assistance.

ACID LAKE RECLAMATION

Acid lakes devoid of fish in the vicinity of Sudbury were selected by the Ministry of the Environment for reclamation through pH adjustment by liming (Michalski and Adamski, 1974). A large number of sediment samples from test and control lakes have been analyzed for nutrients and heavy metals. Large changes in pH and heavy metal distribution down the profile below the sediment-water interface were noted and there were significant differences between test and control lakes and distance from the Sudbury smelters.

SEWAGE TREATMENT PLANT DISPOSAL FIELDS

A monitoring program has been initiated to detect build-up of heavy metals in soil and vegetation in disposal fields associated with sewage treatment plants in Ontario. Digested sludge is also monitored for heavy metals.

SEPTIC TANK DISPOSAL

Soil samples are analyzed for sieving and hydrometer, measurement of the Atterburg plasticity limits and permeability with a view to determining suitability

of soils for septic tank disposal. Extensive studies have been conducted in conjunction with the Applied Science section of the Ministry on phosphate movement away from weeping tile beds. It was found that phosphate soluble in 0.5 N sulphuric acid was a superior indicator of phosphate movement than total phosphorus.

ENVIRONMENTAL IMPACT ASSESSMENT

New legislation requires that a study be made of potential environmental impact prior to any new major program effecting land use, such as the proposed Pickering Airport or new mining activities. These studies often necessitate measurement of a large number of parameters at low levels.

RECREATIONAL LAKES

Sediments and aquatic vegetation samples are analyzed principally for nutrients (total N and P, and Loss on Ignition) in connection with eutophication studies and weed harvesting in recreational lakes throughout the Province.

HAMILTON HARBOUR RESTRATIFICATION

The laboratory is co-operating in a program to improve water quality in Hamilton Harbour by restratification through the injection of air.

INDUSTRIAL SOLID WASTE DISPOSAL

Industrial solid wastes must be acceptable for transport by a carrier and for disposal at a landfill site. The laboratory is frequently asked to determine if various wastes could release toxic leachate. Shake and column leach tests have been devised using various leaching solutions under aerobic or anaerobic conditions, followed by analysis of leachate for parameters such as pH, condutivity and potentially toxic heavy metals (Darcel, 1975). Evaluations are also conducted on proprietary "fixed" solid wastes to test the effectiveness of immobilization of toxic constituents.

INTERNATIONAL JOINT COMMISSION

Large numbers of samples have been received for PLUARG and the Upper Great Lakes surveys as joint programs with state and federal agencies. The Ministry is principally involved in near-shore surveys. Major problems are to attempt to standardize analytical methods used by various state, provincial and federal laboratories with different equipment and capacity capabilities and, where this is not possible, to relate the data obtained by different laboratories.

In such a multi-disciplinary loose organization difficulties are being experienced in resolving which parameters should be analyzed..

The use of .05 N HCl (1-2 gm/200 ml-2 hr shaking) was proposed as an extractant for "available" nutrients and metals in soils (AsIs) by U.S. representatives of the IJC for the 1975 PLUARG Shore Line Erosion Study (Fairless, 1975). "Total" metals were to be analyzed on -10 mesh oven dried material digested in 2:25 ratio with 6N HCl at 100°C for 2 hours.

A large body of data is currently being assembled on the Upper Great Lakes for publication in 1976.

DISPOSAL OF DREDGED SPOIL

The Laboratory has been requested to analyze sediments scheduled for dredging with a view to determining suitability for open water disposal using the criteria established by the Ministry. Areas recently surveyed include the Trent-Severn canal system and Thunder Bay harbour. Consideration is being given to the use of the Elutriate Test of the U.S. Corps of Engineers.

IDENTIFICATIONS

Attempts are made to identify a wide range of materials. Paper and thin layer chromatography procedures were previously used but are time consuming and are being replaced by semi-quantitative spectrographic analysis of solid samples. X-ray diffraction has also been used in co-operation with Dr. J. R. Kramer of McMaster's University, Hamilton. Of interest was

the identification by X-ray diffraction of almost pure crystalline struvite (hydrated magnesium ammonium phosphate) blocking piping at the Lakeview Sewage Treatment Plant.

FUTURE DEVELOPMENTS

With increasing public awareness of environmental hazards and response by government agencies, there is an increasing demand on the laboratory. The role of sediments and soils is becoming increasingly appreciated reflected in the number of samples and tests. No longer is the relatively straight forward total elemental composition analysis sufficient but information is required on chemical species, inorganic and organic complexes and their availability to biota. The importance of the interstitial water and redox measurements in sediments and soils is becoming recognized and the need to measure "free" versus "combined" metals in the aqueous phase interacting with the sediment. The need to isolate and analyze thin layers and hence small samples such as at the sediment-water interface or parts of a plant or animal organs has become a challenge to the analyst.

The detection limit for elements such as cadmium has to be improved by procedures such as pre-concentration by evaporation, ion exchange or solvent extraction prior to AAS.* A continuing challenge is the accurate measurement of trace levels in the presence of high concentrations of metals such as iron, calcium and manganese.

* More recently, an improved detection limit was obtained using the Varian M-1250.

Routes are being explored to perform the large volume of requested analyses as cheaply and rapidly as possible.

Resources are now available within the Ministry's Central Laboratory of sophisticated equipment such as differential pulse anodic stripping voltammetry, mass spectrometry, liquid and gas chromatography and electron microscopy and the necessary expertise to meet the challenge.

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